

# Studies in organic archaeometry IV<sup>1</sup>: analysis of an organic agglutinant used to fix Iron-age clay figurines to their base

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## Abstract

Among many other objects a number of (mainly broken) figurines made of burnt clay were found in a richly furnished Early Iron-age tomb excavated in Lower Austria. Some of these had a dark organic material on their legs, obviously intended to fix the figurines to a base.

A small sample of this agglutinant was analyzed: upon isolation of the characteristic terpene-containing fraction <sup>13</sup>C-nmr spectroscopy showed considerable quantities of betulin. Thus this adhesive can be considered as birch bark pitch.

**Keywords:** Archaeometry, Iron-age figurines, agglutinant, <sup>13</sup>C-nmr spectroscopy, birch bark pitch

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## Introduction

In 1981 an Early Iron-age Tumulus of the eastern Hallstatt-culture (about 600 b.c.) with rich grave furnishings ("prince-burial") was discovered in Langenlebarn, District of Tulln, Lower Austria, and excavated by the *Department of Archaeological Monuments* of the *Austrian Federal Office for the Protection of Historical Monuments* (Abteilung für Bodendenkmale des Bundesdenkmalamtes), directed by Johannes-Wolfgang Neugebauer.

The findings of this grave are currently studied by one of us (Fritz Preinfalk) within a diploma thesis at the Institute for Prehistory at the University of Vienna.

Apart from some smaller bronze objects the cremation burial contained 38 richly decorated, mostly red and black painted clay vessels. Two among them are of particular significance: a pot equipped with two bovine heads and a kernos-like vessel (conically necked vessel with three small pots set on the rim), as they could be considered – in a wider sense – as objects with a religious function.

The same is true for a number of (mostly fragmented) figurines made from burnt clay which were also found in this grave: a horseman with a shield (picture 1),



**Picture 1<sup>2</sup>.** Clay figurine of a horseman (total height:9,8 cm, length of the horse: 8,7 cm).

at least seven human figurines and five horses. Some of them have lumps of a dark organic material on the lower part of their legs (picture 2) which obviously was used to fasten the figurines to an unknown (maybe wooden) base.



**Picture 2<sup>2</sup>**. Detail of picture 1, showing parts of the legs with the organic adhesive.

A small sample of this material (which was already broken away from one of the figurines) was used for chemical analysis. This should show whether or not this agglutinant is identical with the material which was used for many purposes in prehistoric central and northern Europe, i.e., whether or not it is birch bark pitch<sup>3</sup>.

The analytical method applied was one published by us recently<sup>4,5</sup>, which is mainly based on isolation of the significant terpene-containing fraction, ensued by <sup>13</sup>C-nmr spectroscopy (c.f. Experimental).

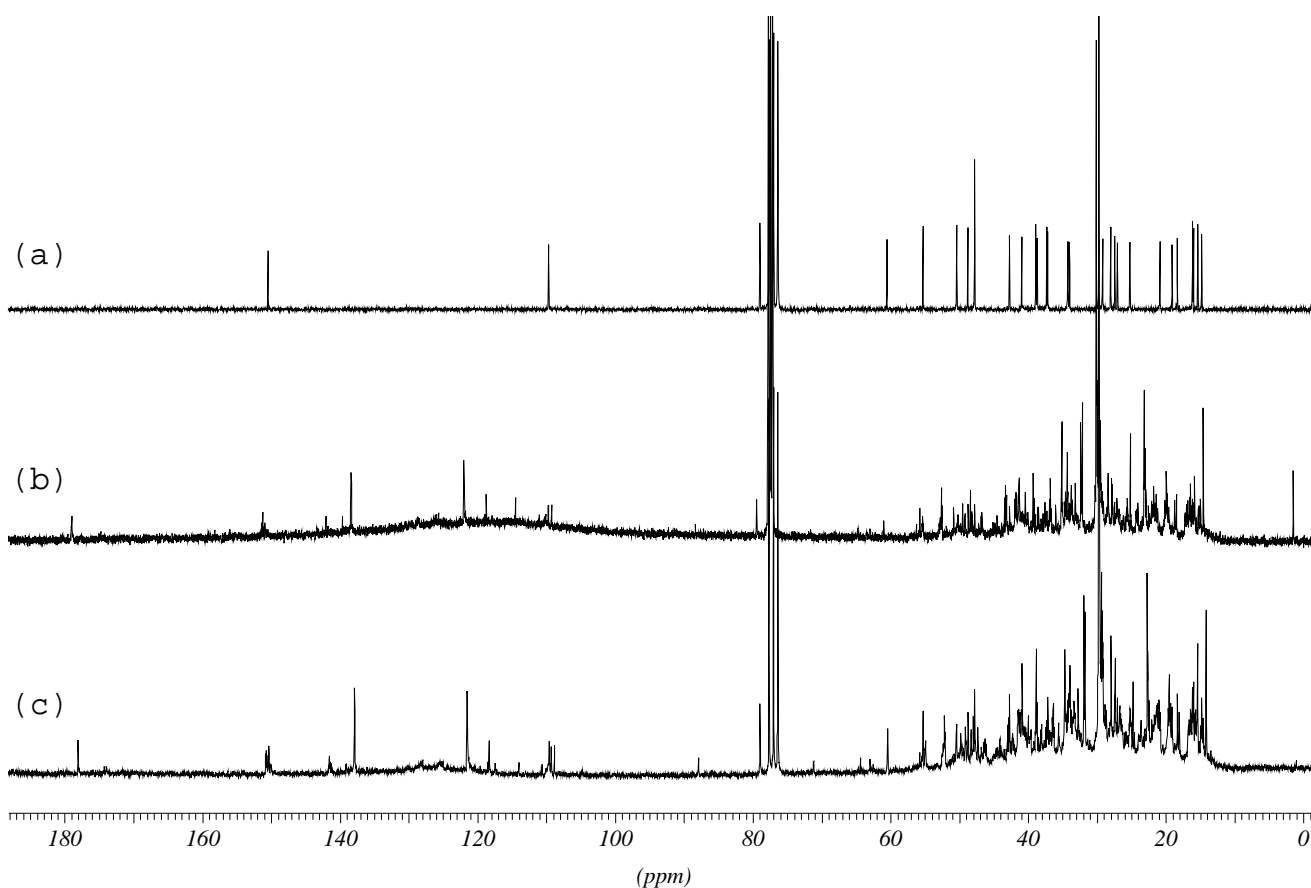
## Experimental Section

Analysis of the products in question:

A small sample was distilled in a Kugelrohr under reduced pressure (slow heating up to 300°C, 22-25 mbar) to isolate the characteristic terpenoid fraction. 40 mg of this material was dissolved CDCl<sub>3</sub> and studied by <sup>13</sup>C nmr spectroscopy (Bruker DRX400 FT nmr spectrometer, 5 mm inverse broadband probehead, approx. 60000 scans, shifts relative to TMS).

## Results

The following overview shows <sup>13</sup>C nmr spectra of (a) pure betulin, (b) a sample of the material in question, and (c) a material known as birch bark pitch, containing a large amount of betulin.



The spectrum of the analyzed material shows the characteristic pattern of terpenoid compounds with their large number of signals in the aliphatic region (15 to 50 ppm), and - more important - a detailed analysis unambiguously shows the presence of a certain amount of betulin in the compound of interest.

## Conclusions

The dark organic substance contains substantial quantities of betulin.

**It thus can be considered to be the same material as was found frequently in prehistoric central and northern Europe, i.e. it can be considered to be birch bark pitch.**

## References

1. Our earlier papers in this ARKIVOC series:
  - 1.1. Studies In *Organic archaeometry I*, Fritz Sauter, Ulrich Jordis, Aloisia Graf, Wolfgang Werther and Kurt Varmuza, Identification of the prehistoric adhesive used by the "Tyrolean Iceman" to fix his weapons, *ARKIVOC 2000*, (v).
  - 1.2. Studies In *Organic Archaeometry II*, Fritz Sauter, Leopold Puchinger, Aloisia Graf and Diane Thumm, Analysis of the ancient content of a flask excavated in Troia, *ARKIVOC*, in press
  - 1.3. Studies In *Organic Archaeometry III*, Fritz Sauter, Aloisia Graf, Christian Hametner, and Johannes Fröhlich, Prehistoric adhesives: alternatives to birch bark pitch could be ruled out, *ARKIVOC*, in press
2. Photo: Chr. Neugebauer-Maresch, reproduction with permission of Museum of Natural History in Vienna, Prehistoric Dept.
3. Some literature dealing with prehistoric pitches and analyses thereof: c.f. review by Jürgen Weiner, European Pre- and Protohistoric Tar and Pitch: A Contribution to the History of Research 1720, *Acta Archaeometrica* (Libavius Verlag Coburg, Germany) **1999**, 1, 1.
4. Hametner, C.; Fröhlich, J.; Sauter, F.; Graf, A. Archaeometric Investigations of Prehistoric Pitches and Tars by  $^{13}\text{C}$ -NMR Spectroscopy, Abstracts of the *13th Meeting of the Central European NMR Discussion Groups*, (27-29 April, 1998, Valtice, Czech Republic)
5. Fröhlich, J.; Hametner, C.; Sauter, F.; Graf, A. Identifizierung von Betulin in prähistorischen Pechfunden mittels  $^{13}\text{C}$ -NMR-Spektroskopie, *Berliner Beiträge zur Archäometrie* **16 1999**, 241.